# RAMAN FREQUENCIES OF HDO*

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Plate VII

**ABSTRACT.** Mixtures of water and heavy water in two proportions 1 : 9 and 9 : 1—are studied. The Raman frequencies of HDO inferred from the spectra are 2523 and 3363. These results are compared with data available hitherto. Changes in the structure of the $H_2O$ and $D_2O$ bands are also explained.

## INTRODUCTION

In the study of the Raman spectrum of a mixture of water and heavy water by I. R. Rao and the author,[1] it was observed that the intensity of the $D_2O$ band in the mixture increased by 50% from the pure liquid, while the $H_2O$ band did not show any corresponding increase. This fact was explained as due to the formation of HDO molecule in the mixture. The Raman frequencies of HDO are not known with any certainty. Wood[2] who studied 18% and 80% mixtures concluded that HDO has two Raman frequencies of 2623 and 3445; but his studies with the vapour [2a] do not give any indication of the frequency of HDO corresponding to the OH oscillation. Rank, Larson and Bordner,[3] who also studied the Raman spectrum of the vapour of a mixture of water and heavy water, could report only a frequency of 2718 cm.$^{-1}$ for HDO in the vapour state. The results of these investigators regarding the absence of any OH oscillation for vapour are very interesting. Our results with the 50 : 50 mixture of $H_2O$ and $D_2O$ also showed a difference in the $H_2O$ and $D_2O$ bands in the mixture. We were hence led to investigate mixtures most suitable for recording the Raman frequencies of DOH, without the superposition of $D_2O$ and $H_2O$ bands.

Urey and Rittenberg[4] have calculated the equilibrium constant for the reversible reaction, $H_2O + D_2O \rightleftharpoons 2HDO$ as 3.28. According to this the smaller the proportion of $H_2O$ or $D_2O$ in the mixture, the greater will be the percentage of HDO molecules compared to $H_2O$ or $D_2O$ respectively. If the proportion of HDO is very much greater compared to $H_2O$ or $D_2O$, it will be possible to get the band due to HDO without the bands due to $H_2O$ or $D_2O$ overlapping it. But the proportion of $H_2O$ or $D_2O$ cannot be made too small. If the quantity of HDO in the mixture be small, unduly long exposures would be needed. Hence two mixtures of $H_2O$ and $D_2O$ in the ratios 1 : 9 and 9 : 1 (by volume) are chosen for study. Table I gives the proportion of $H_2O$, $D_2O$ and

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HDO molecules in these mixtures. The corresponding proportions for the mixtures studied by R. W. Wood[2] are also given there.

TABLE I

| | Mixture | | $D_2O$ | $H_2O$ | DOH |
|---|---|---|---|---|---|
| Author's | (i) $H_2O : D_2O$ | 1 : 9 | 81.9 | 1.1 | 17.8 |
| | (ii) $H_2O : D_2O$ | 9 : 1 | 1.1 | 81.9 | 17.8 |
| Wood's[2] | 80% mixture | | 64.0 | 4.0 | 32.0 |
| | 18% mixture | | 3.4 | 66.0 | 30.0 |

It is evident that the mixtures used by the author are better suited for the study of HDO frequencies than those of R. W. Wood.

## EXPERIMENTAL

The apparatus used is similar to that adopted in the studies of the 50 : 50 mixture. Only the Wood's tube used is of a smaller capacity of 50 c.c. Since it is our object to study the Raman spectrum of HDO, the spectra of the pure liquids are not recorded. The liquids are very carefully distilled in vacuum, so as to be free from dust. A close arc arrangement together with a glass spectrograph of high light-gathering power is used to photograph the spectra. With this arrangement an exposure of about 10 hours was enough to get fair records of the HDO bands. Longer exposures which would have given more intense pictures could not be availed of, on account of the unavoidable reflection of light from the sides of the Wood's tube, since it had a small cross section. The bands excited by the 4046 line of the mercury arc are chosen for study. The spectra are microphotometered and the frequencies of the HDO bands are measured by extrapolating from these curves, with the mercury lines as the standards.

## RESULTS

The microphotometric curves corresponding to the two spectra taken with 9:1 and 1:9 proportions of $D_2O$ and $H_2O$ are reproduced in Fig. 1 (Plate VII). The band corresponding to the HDO oscillations excited by the 4046 line of the mercury arc are marked by arrows. The lower curve corresponds to the spectrum taken with the mixture containing excess of $D_2O$, and the upper curve to that with a mixture containing excess of $H_2O$. The curves clearly indicate that the band due to HDO appearing in the position of the pure $D_2O$ band is much sharper than that in the position of the $H_2O$ band. Only one of the frequencies due to HDO is recorded in either picture as the band due to the liquid in excess obscures the second HDO frequency lying in that region. In each case, the principal

band due to the liquid in excess shows some minor changes which are to be expected from the presence of a second substance in the mixture. These changes are similar to those found in very dilute solutions.

## DISCUSSION

The table given in the introduction shows that the number of HDO molecules in $H_2O$ : $D_2O = 1:9$ mixture is nearly sixteen times the number of $H_2O$ molecules. The proportion of $H_2O$ molecules in the whole mixture is less than two per cent. Hence the band occurring in the region of the $H_2O$ band must be mainly due to HDO and not to $H_2O$. Similarly the band in the position of the pure $D_2O$ band in the mixture with excess of water cannot have its origin in $D_2O$, but must also be assigned to HDO. The frequencies of the maxima of these two bands are 3363 cm.$^{-1}$ and 2523 cm.$^{-1}$. The former frequency shows that HDO has a frequency corresponding to the OH oscillation and the failure of Wood[2] and Rank, Larson and Bordner[3] to get it in the vapour is perhaps accidental. The Raman frequencies assigned by the various workers to the HDO molecule are shown in Table II. The frequencies given by the author also refer to the

TABLE II

| Author | Frequencies in cm$^{-1}$ | | |
|---|---|---|---|
| | (*i*) | (*ii*) | (*iii*) |
| R. W. Wood[2] | 3445 (Liquid) | 2623 (Liquid) | — |
| Rank, Larson, Bordner[3] | — | 2718 (Vapour) | — |
| Van Vleck, Cross[5] (calculated) | 3750 | 2720 | 1400 |
| Author | 3363 | 2523 | — |

liquid state. There is a large difference between the frequency given by Wood (2623) and the corresponding value of the author (2523). Wood did not measure from microphotometer records, and the proportion of HDO to $D_2O$ is greater in the mixtures studied by the author, and these values are therefore more reliable.

The frequencies 2523 and 3363 cm.$^{-1}$ of the maxima of the Raman bands of HDO are smaller than those of $D_2O$ and $H_2O$ which are 2538 and 3443 cm.$^{-1}$ respectively. The decrease in the frequencies of both OH and OD oscillations in HDO from those in $H_2O$ and $D_2O$ respectively is difficult to explain. HDO results by substituting one of the hydrogen atoms in $H_2O$ by a heavier isotope or one atom of heavy hydrogen in $D_2O$ by the lighter isotope. That both these changes should result in a similar change (decrease) in the frequency is very interesting. Substitution of an atom by a heavier isotope in the molecule should diminish the

frequency of any particular oscillation. The change in the frequency of the OH follows this rule, while the OD oscillation does not obey it, since it is expected that the frequency should increase when one of the atoms diminishes in mass. The frequency corresponding to the OH oscillation is much further away from that in $H_2O$ than the corresponding OD oscillation from that in $D_2O$. The influence of the D atom on OH oscillation seems to be much more than that of the H atom upon the OD oscillation, as seen in the greater change of the OH frequency in DOH. This may be due to the heavier mass of the D atom.

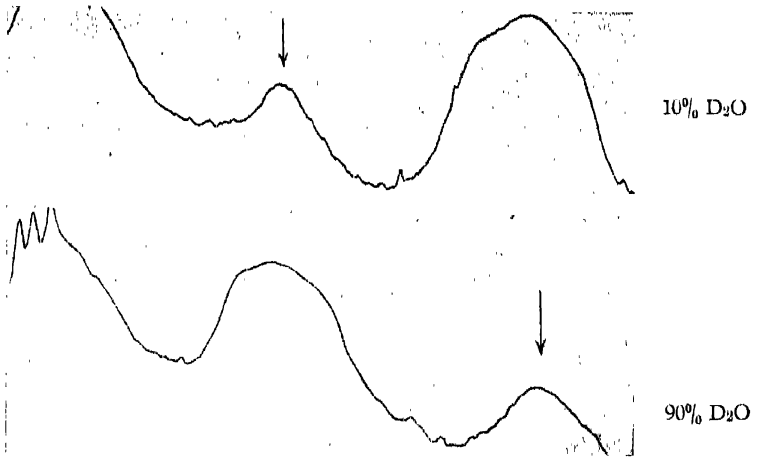
In the discussion on the 50 : 50 mixture[1] it is pointed out that the HDO frequency in the region of the $D_2O$ band is likely to be less than the frequency of $D_2O$ band. The displacement of the $D_2O$ band in the mixture towards the Rayleigh line must be due to the superposition of the DOH band. Though the HDO frequency in the region of $H_2O$ band is also less than that of pure $H_2O$, in the 50 : 50 mixture the maximum of the $H_2O$ band is not displaced in the direction of the HDO frequency.

The Raman frequencies of HDO, like those of $D_2O$ and $H_2O$, are broad and diffuse. The extent of the 2523 cm.$^{-1}$ frequency is 200 cm.$^{-1}$ while that of the 3363 frequency is 490 cm.$^{-1}$. Thus the latter is broader by more than two times.* The width of the principal bands of pure $D_2O$ is nearly 650 cm.$^{-1}$ and that of pure water 850 cm.$^{-1}$. These widths are in the ratio of their frequencies (maxima of the bands) as required by the isotopic substitution. In the case of DOH, however, the 2523 band is less broad (less than half) and sharper than the 3363 band. This cannot be explained merely on the basis of the difference in the reduced masses in the case of the two oscillations. It must be interrelated with the greater change in the frequency of the OH oscillation.

No band corresponding to the 1400 cm.$^{-1}$ is recorded. This band, if present, must be much less intense than the other two. The 1600 cm.$^{-1}$ band observed in water or the 1200 band in heavy water is much feebler than the principal bands. On this basis, it may be inferred that 1400 cm.$^{-1}$ of HDO is also very weak and much stronger impression than obtained here may be necessary to record it. The diffuseness and the breadth of the bands of HDO like those of water and heavy water indicate that they have a structure similar to that of $H_2O$ or $D_2O$ bands. Evidence about this can be obtained only by studying the temperature effect. A preliminary study with the $H_2O : D_2O = 9 : 1$ mixture indicates a shift in the maximum of the 2523 band to 2543 at 80°C. This is similar to the effect observed in water and heavy water by I. R. Rao[6] with increase of temperature.

The microphotometer record of the Raman spectrum of the mixture containing excess of water shows also the principal band of $H_2O$. It shows

* The limits of the 2523 and 3363 bands are respectively 2433 and 2643, and 3113 and 3603 cm.$^{-1}$.




Microphotometric record of the Raman spectra of the mixture of $H_2O$ and $D_2O$.

the diminution in the intensity of the shorter frequency component as compared to the pure liquid. The effect is not as pronounced as in the case of the 50 : 50 mixture. It is similar to the effect observed with increase of temperature or in solutions. This may be explained as due to a change in the equilibrium between the three types of structures responsible for the three components. According to I. R. Rao,[6] the shortest frequency component is due to triple polymers and in the mixture a fraction of the trihydrols is depolymerised. Similar changes in the heavy-water band in the mixture containing excess of heavy water are observed. They have a similar explanation based upon the splitting up of the triple polymers of heavy water. If the three structures proposed by Bernal and Fowler[7] are adopted, the structure of water or heavy-water in the mixtures containing them respectively in excess, must be reckoned as approximating less to type I (like tridymite) and more to type II (like quartz) than in the pure liquids. These changes are to be expected from the other components in each mixture. The mixture is only a solution and the changes found here are similar to the effect of dissolved substances upon the solvent.

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